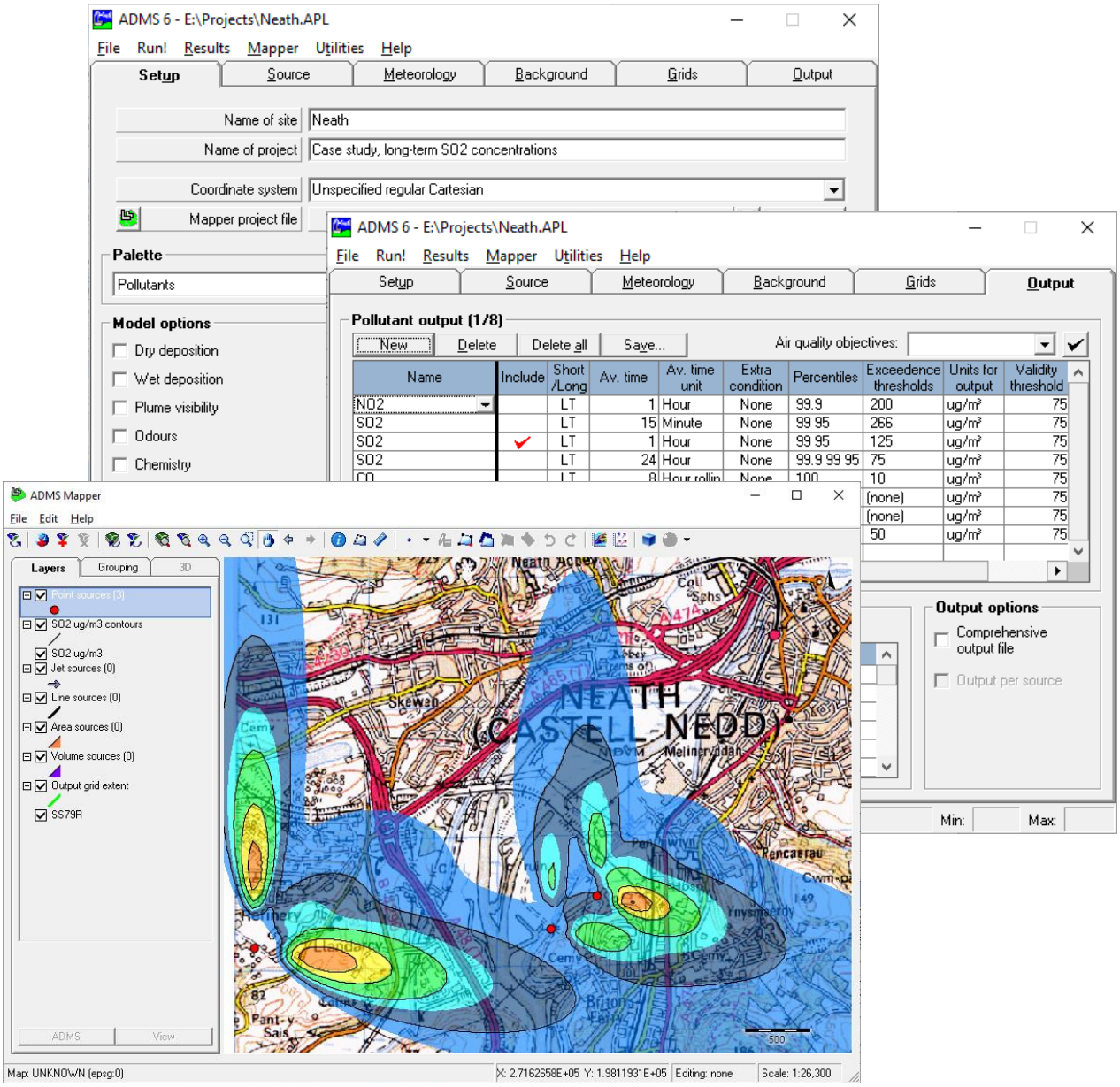
ADMS 6

Amine chemistry supplement



User Guide CERC

ADMS 6

Amine chemistry

User Guide Supplement

Version 6.0

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SECTION 1 Introduction

ADMS 6 contains an amine chemistry scheme as an extension to the NO_x chemistry scheme. The modelling of amine chemistry can be important in assessing the impacts of emissions due to amine-based carbon capture. In these activities the amine solvent is recycled, but some of the amine can be lost via the stack. These amines can react with other species in the exhaust gas and the atmosphere to produce degradation products (nitrosamines and nitramines) that can be harmful. Recommendations from the Norwegian Institute of Public Health (NIPH) (Lag *et al.*, 2011) indicate that the annual average of the sum of nitrosamines and nitramines should not exceed 0.3 ng/m^3. The main reaction of amines in the atmosphere is with hydroxyl radicals and it is this reaction on which the amine chemistry scheme is based.

An overview of the amine chemistry scheme in ADMS 6 is given in this section together with instructions on how to install the amine chemistry module in ADMS 6. Section 2 then describes how to implement the scheme in a model run, a technical summary is given in Section 3 and Section 4 lists the references.

This document should be read in conjunction with the main ADMS 6 User Guide.

1.1 Overview of amine chemistry

ADMS 6 incorporates an amine chemistry scheme which treats the reactions initiated by the attack of an emitted gaseous amine by a hydroxyl radical ($^{\bullet}OH$), and the subsequent formation of nitrosamines and nitramines. This chemistry scheme can be applied to a variety of amines, including primary, secondary and tertiary amines and is based on the one outlined in an Atmospheric Degradation of Amines (ADA) report (Nielsen *et al.*, 2011), published by the Norwegian Institute for Air Research (NILU) as part of the Climit project.

The general reaction scheme is shown below, where R represents an alkyl group and the terms in capitals are the text part of the generic names used by the model:

AMINE + $^{\bullet}OH$	→	amino RADICAL + H_2O	(1a)
	→	$RN(H)C^{\bullet}H_2$ + H_2O	(1b)
amino RADICAL + O_2	→	imine + HO_2	(2)
amino RADICAL + NO	→	NITROSAMINE	(3)
amino RADICAL + NO_2	→	NITRAMINE	(4a)
	→	imine + HONO	(4b)
NITROSAMINE	hv →	amino RADICAL	(5)

The reaction rates and kinetic parameters for the various species must be specified by the model user and each can be varied independently. The way in which these parameters are specified is described in Section 2.1

The reaction scheme also involves nitrogen oxides and ozone, so modelling will require NO_x emissions and background concentrations, and ozone background concentrations. It uses information from the ADMS meteorological processor to determine photolysis rates on an hourly basis. In particular, the hydroxyl radical concentration is determined from the ambient ozone concentration and the photolysis rate constant for nitrogen dioxide.

Additional options are available to take into account the absorption of the amines, nitramines and nitrosamines into liquid water within the plume (Section 2.3) and for taking into account the effects of rainfall induced washout of amines and their products on their airborne concentrations (Section 2.4).

In addition to the implementation of the amine chemistry reactions within the ADMS 6 model code, there is an option to improve the way that the chemistry module takes into account the effects of the dilution of pollutant species and the entrainment of background pollutants. Although this 'dilution and entrainment' effect can be switched on and off by the model user, it is strongly recommended that it is switched on for all model runs involving amine chemistry, refer to Section 2.1 for instructions.

1.2 Installing the amine chemistry option in ADMS 6

Before the amine chemistry option can be used in ADMS 6 you must first update the Additional Input file editor so that the amine chemistry option is available. To do this, ensure you are logged onto the computer as Administrator and then navigate to the *<ADMS 6 install directory>\Support\AAI Editor\Syntax With Amine* directory and run *ToEnglish.bat*.

In addition, you must have purchased and installed a valid licence (*.lic*) file for this option. To install the licence file first make a back-up copy of any *ADMS.lic* file in your ADMS 6 install directory and then copy and paste your new licence file to the install directory, ensuring its named *ADMS.lic*.

1.3 Upgrading from ADMS 5

1.3.1 Changes since ADMS 5

ADMS 6 includes a number of additional features when modelling amine chemistry compared to ADMS 5. These features are:

1. The ability to model multiple point sources in the same run when using the low concentration dilution and entrainment option. The chemistry for each source is still modelled individually with the results then recombined for the final concentration;

2. The ability to model multiple amine species within the same run. These species can have different kinetic parameters and emission rates;

3. The ability to take into account the absorption of amines and their products into liquid water within the plume, including a new option to calculate plume liquid water content based on nucleation around salt particles;

4. The ability to take into account the effects of rainfall on the airborne concentration of amines and their products;

5. It is no longer necessary to add the amine radical to the pollutant palette, unless output of the radical is required; and

6. The atmospheric oxygen content is no longer a user input.

1.3.2 Steps to upgrade existing model run files from ADMS 5

Once ADMS 6 has been installed including the amine chemistry option, Section 0, there are several steps necessary to upgrading existing *.apl* files to ADMS 6 format. The steps for this are described below:

1. Open the existing *.apl* file in the ADMS 6 interface. You should see a warning that the file will be upgraded, **Figure 1**. Click **Yes** to continue.

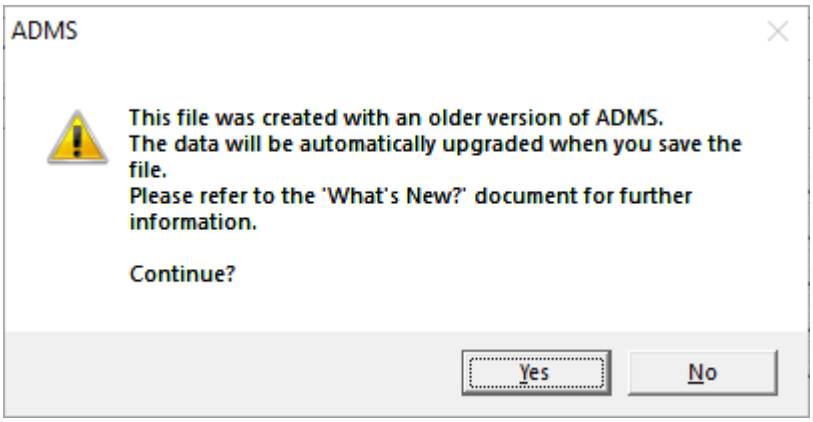

Figure 1: Warning regarding updating .apl from older file format.

2. On the **Setup** screen open the **Palette of pollutants** by clicking on the **Data**... button in the **Palette** section. Select the AMINE entry then click **Rename** to change the name to AMINE1. Similarly rename NITRAMINE to NITRAMINE1 and NITROSAMINE to NITROSAMINE1. If RADICAL output is required rename RADICAL to RADICAL1 otherwise this pollutant can be deleted from the **Palette of pollutants**.
3. Click **OK** to close the **Palette of pollutants**.
4. Click **Edit** in the **Additional input file** section to edit the additional input file. You will again get a warning about upgrading from an older format. Click **Yes** to continue.
5. The **Additional input file** editor will open and any existing sections in the additional input file will have been kept except for the **Amine chemistry** section.
6. Enable the **Amine chemistry** section and enter the **Constant for OH concentration calculations**, see Section 2.1.1.
7. Go to the **Amine species** section, click **New** to add a new species then **Edit** to open the screen for that species. Enter AMINE1 as the species name and then enter the kinetic parameters for this amine, see Section 2.1.2.
8. In the **Additional input file editor** select **File**, **Save as** to save the additional input file under a new name.
9. In the ADMS 6 interface, enter the path to this new additional input file using the **Browse**... button in the **Additional input file** section.
10. In the ADMS 6 interface select **File**, **Save as** to save the *.apl* file under a new name.

SECTION 2 How to enable the amine chemistry scheme in ADMS 6

The specific inputs and steps needed to model amine chemistry in ADMS 6 are described in this section. All other model inputs are entered as for a standard ADMS 6 run.

The first stage is to specify the kinetic parameters for the various reaction equations. This is done via the additional input (*.aai*) file which can be easily created with the Additional Input file editor utility in ADMS 6. This is described in Section 2.1.

The second stage is to select the chemistry model option; to enter information into the palette of pollutants for each of the amine, nitrosamine, nitramine and radical species; and to enter the emissions data, background data, and output options for the model run. This is described in Section 2.2.

The option for calculating the effects of absorption of amines and their products into the liquid water of the plume is described in Section 2.3. Section 2.4 describes the option to include the effects of rainfall induced washout on airborne concentrations of amines and their products.

Additionally, some modelling tips are given in Section 2.5.

2.1 Setting up the additional input (*.aai*) file

This section describes how to specify the kinetic and other parameters for the reaction scheme via the additional input (*.aai*) file.

2.1.1 Modelling amine chemistry

To launch the Additional Input file editor, open the ADMS 6 model interface, check the box in the **Additional input file** section of the **Setup** screen and then click on **Edit**. The screen should be as shown in **Figure 2**.

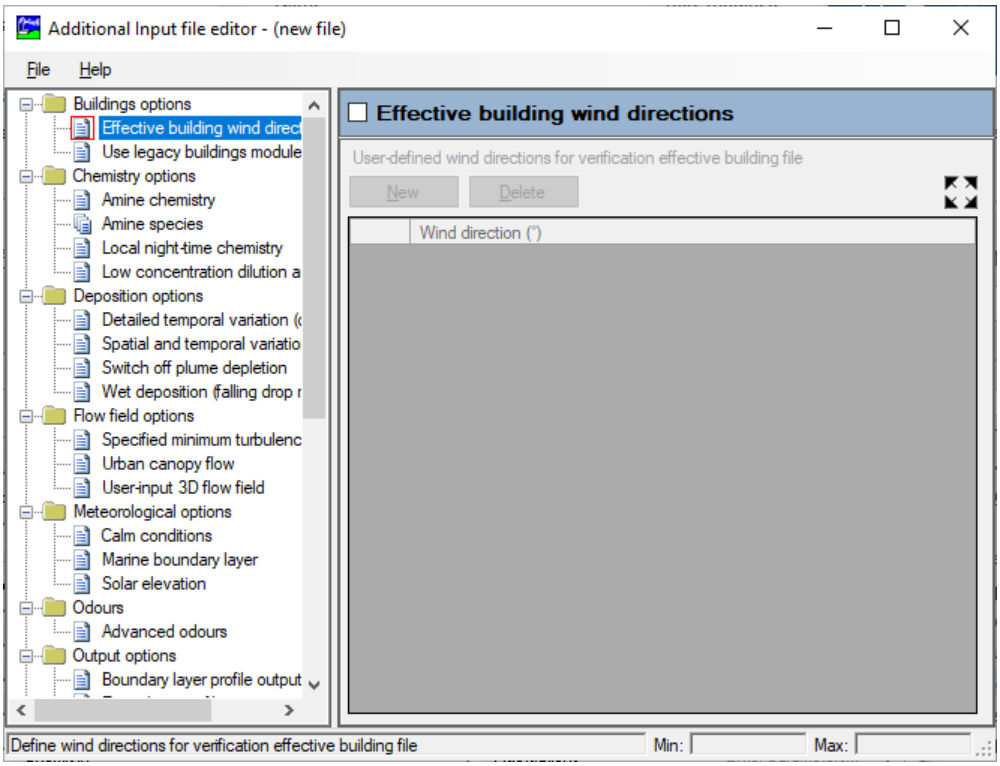

Figure 2: **Additional Input file editor**.

In the Additional Input file editor, select **Amine chemistry** under **Chemistry options** from the menu on the left hand side of the screen. Then check the box next to **Amine chemistry** in the main window of the Additional Input file editor. The cells for the various other parameters are no longer greyed out, as shown in **Figure 3**. There is one mandatory parameter which must be entered:

- **Constant for OH concentration calculations**, the constant, c, for the hydroxyl radical concentration calculations, in units of seconds. A value for c can be estimated from known typical values of $[O_3]$, $[OH]$ and j_{NO_2}, refer to Section 2.5 for further details.

There are also two optional settings:

- **Amines washout**, calculate the effect of rainfall induced washout on the concentrations, see Section 2.4.
- **Aqueous amine scheme**, calculate the effect of uptake of the amine species into liquid water within the plume, see Section 2.3.

Once this section has been completed it is necessary to provide details on the kinetics of the amine species.

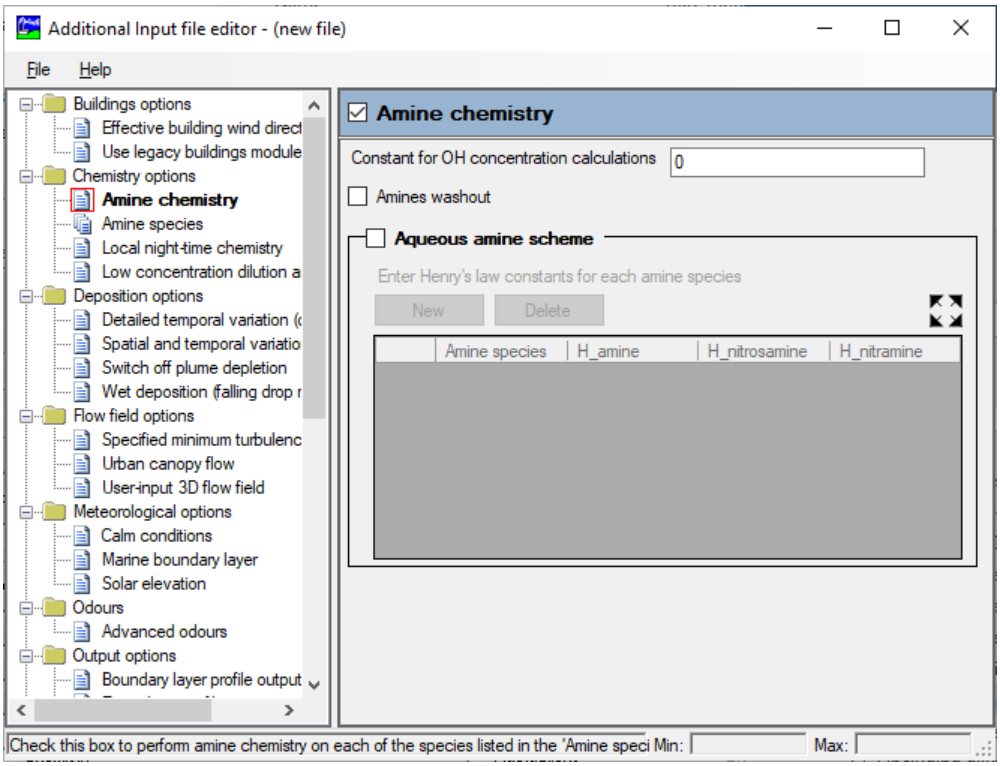

Figure 3: **Amine chemistry** section of the **Additional Input file editor**.

2.1.2 Specifying the kinetic parameters

In the Additional Input file editor, select **Amine species** under **Chemistry options** from the menu on the left hand side of the screen, **Figure 4**. Up to nine amine species can be added by clicking the **New** button. The parameters for these species are entered by clicking on the **Edit** button and existing species can be deleted via the **Delete** button.

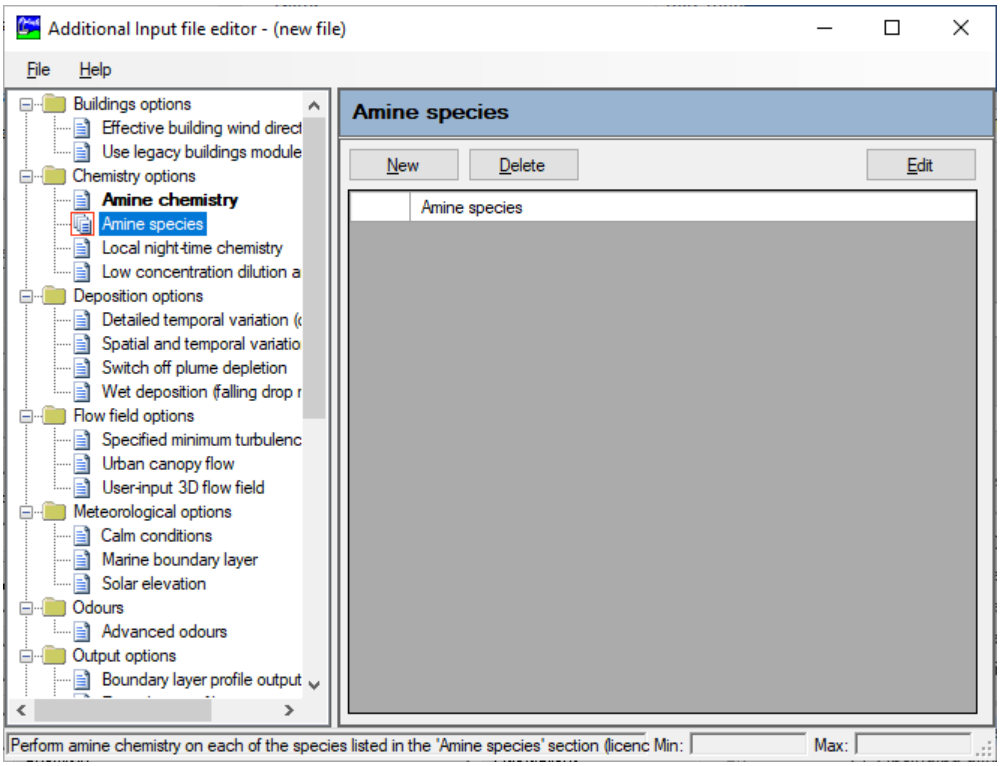

Figure 4: **Amine species** section of the **Additional Input file editor**.

Clicking on the **Edit** button brings up the screen for specifying the kinetic parameters for this amine species. Values for each of the parameters are entered in each cell as appropriate. In order, the values are:

- **Amine species name**, the name of the amine species as used in the ADMS 6 interface. Must be in the form 'AMINE#' where # is a single digit number between 1 and 9, see Section 2.2.1 for more details on the naming convention.

- **Amine/OH reaction rate constant**, the rate constant for the reaction of the amine with the hydroxyl radical, k_1, in units of $ppb^{-1}s^{-1}$;

- **Amino radical/O2 reaction rate constant**, the rate constant for the reaction of the amino radical with oxygen, k_2, in units of $ppb^{-1}s^{-1}$;

- **Rate constant for formation of nitrosamine**, the rate constant for the formation of nitrosamine, k_3, in units of $ppb^{-1}s^{-1}$;

- **Rate constant for formation of nitramine**, the rate constant for the formation of nitramine, k_{4a}, in units of $ppb^{-1}s^{-1}$;

- **Amino radical/NO2 reaction rate constant**, the rate constant for the reaction of the amine radical with NO_2, k_4, in units of $ppb^{-1}s^{-1}$;

- **Branching ratio for amine/OH reaction**, the branching ratio for the amine/hydroxyl radical reaction, $\frac{k_{1a}}{k_1}$, this is dimensionless;

- **Ratio of J(nitrosamine) to J(NO2)**, the ratio of the photolysis rate constants for the

nitrosamine and NO_2, $\frac{j_5}{j_{NO_2}}$, this is dimensionless;

You may find it helpful to refer to the reaction equations in Section 3 for details of the chemistry scheme.

Care should be taken to ensure that the rate constants are entered in the correct units. To convert from $cm^3mol^{-1}s^{-1}$ to $ppb^{-1}s^{-1}$ multiply by a factor of $2.5*10^{10}$.

There is also an option to specify that only unstable nitrosamines are created, **Creation of unstable nitrosamines**. If this option is selected, the nitrosamine concentrations are always set to zero. This should usually be left unchecked unless the amine being modelled produces unstable nitrosamines. This tends to be the case for primary amines, for which the nitrosamine formed rapidly isomerises to form an imine.

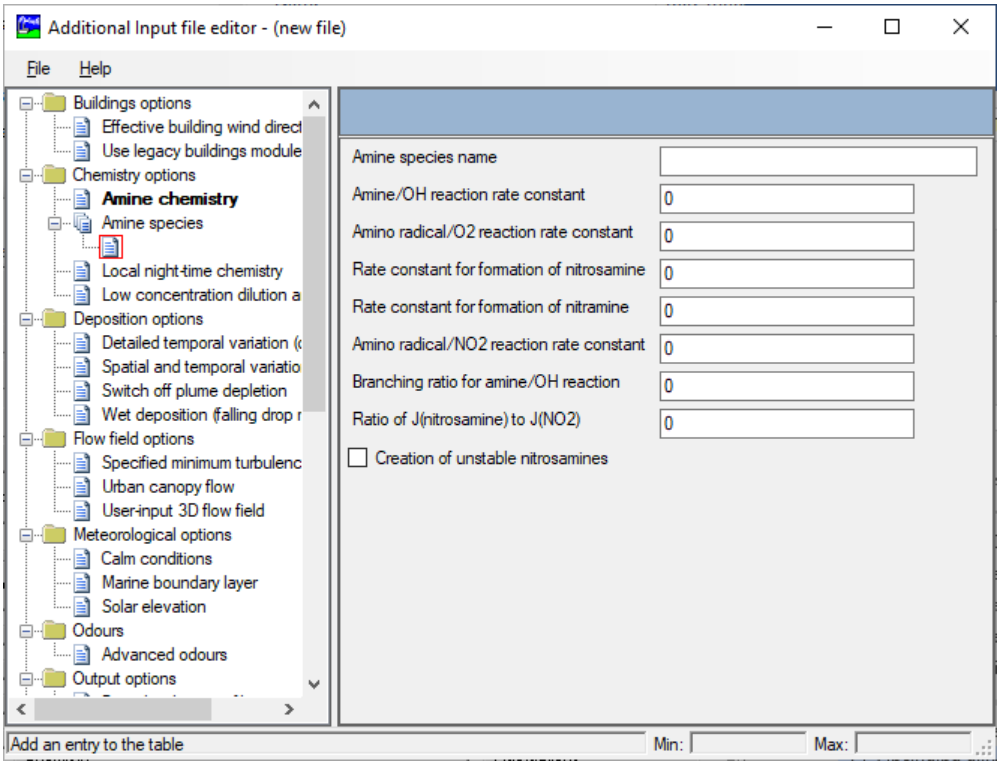

Figure 5: Species specific details in the **Amine species** section of the **Additional Input file editor**.

2.1.3 Including dilution and entrainment effects

As mentioned in Section 1, there is an option to improve the way that the chemistry module takes into account the effects of the dilution of pollutant species and the entrainment of background pollutants.

When modelling amine chemistry it is strongly recommended that this option is selected as this option is especially important when there are very low concentrations of chemical species.

To include this option, click on **Low concentration dilution and entrainment** in the **Chemistry**

options menu, this is found on the left hand side of the Additional Input file editor screen. Click the check box next to **Low concentration dilution and entrainment** to select this option, see **Figure 6**.

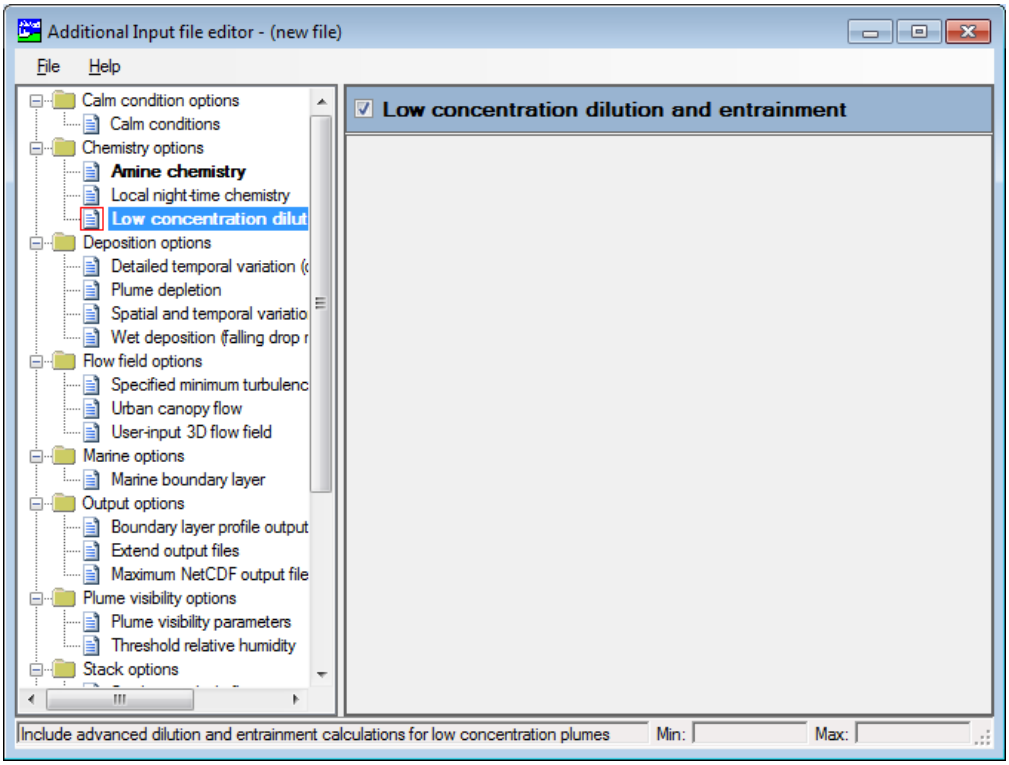

Figure 6: The **Low concentration dilution and entrainment** option.

When all the options in the Additional Input file editor have been selected and filled in as appropriate click on **File**, **Save** to save the additional input (*.aai*) file. Close the Additional Input file editor. Then in the **Setup** screen of the ADMS 6 interface click on **Browse...** in the **Additional input file** section to specify the file path of the *.aai* file just created, which contains the data for the amine chemistry scheme.

2.2 Setting up the ADMS interface

Additional data is required for the **Setup**, **Source**, **Background** and **Output** screens of the ADMS 6 interface when modelling amine chemistry. These are each described in turn in this section.

2.2.1 Setup screen

The first step is to select the **Chemistry** option in the **Setup** screen of the ADMS 6 interface, see **Figure 7**. To do this, click the check box next to **Chemistry**.

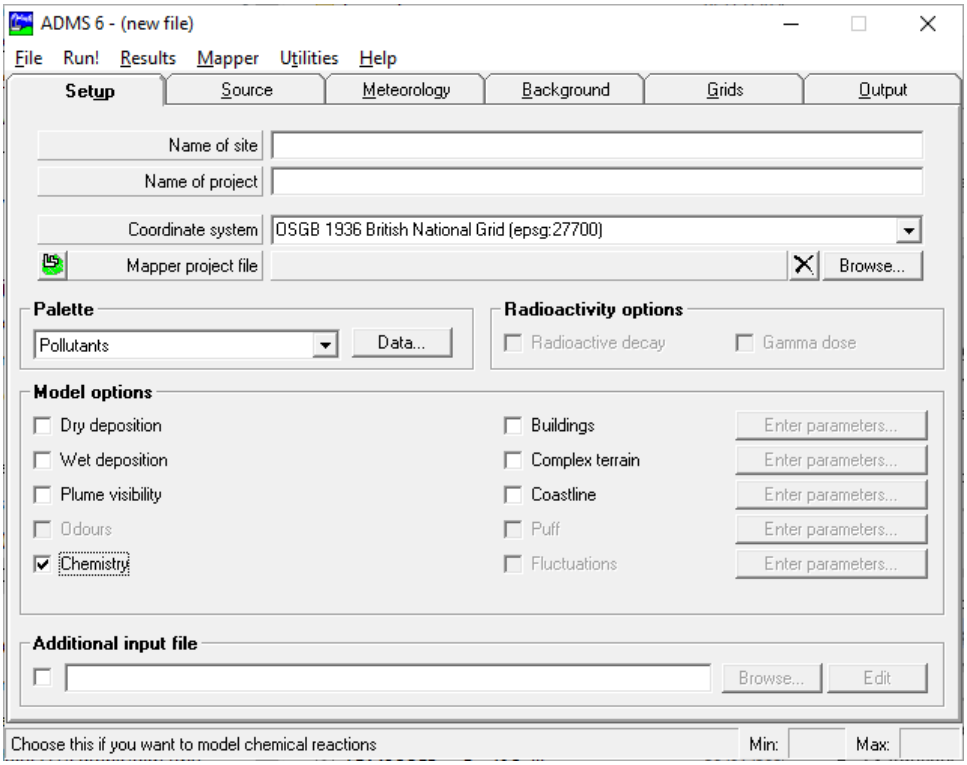

Figure 7: The **Setup** screen with the **Chemistry** option selected.

Next, the file path of the additional input (*.aai*) file that contains the data for the kinetic and other parameters must be specified. To use an additional input file, check the box in the **Additional input file** section and then enter the path to the file or click on **Browse**... to browse to find the file, see **Figure 8**.

*Neither **Dry deposition** nor **Wet deposition** should be selected if the amine chemistry scheme is being used. A method for calculating the deposition of amine and its products is given in Section 2.5.2.*

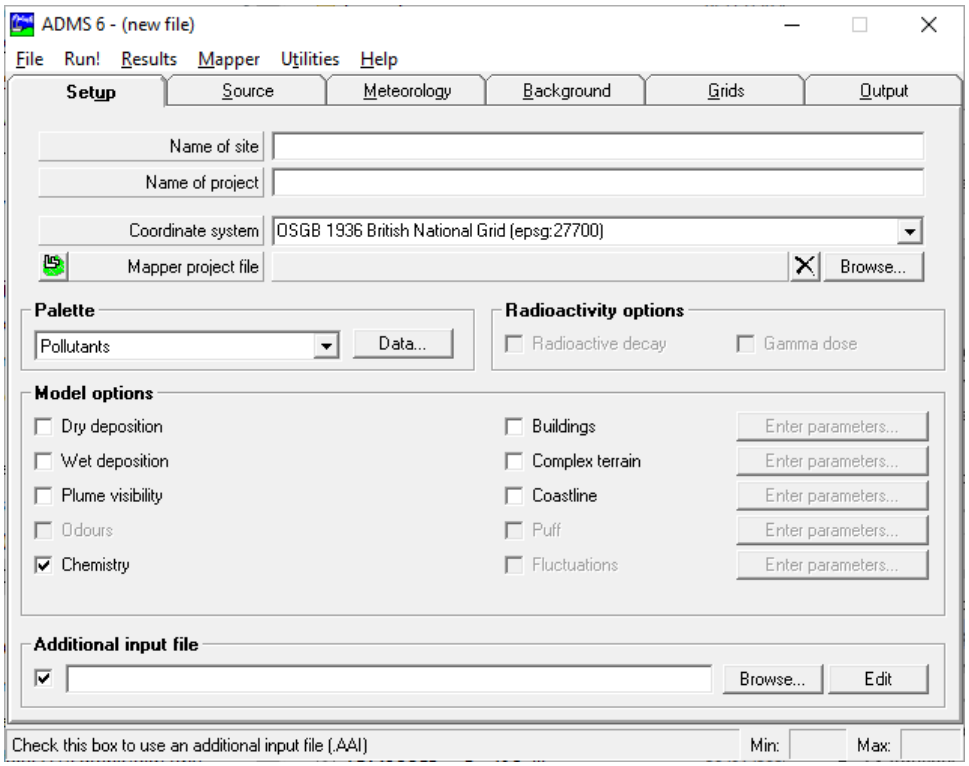

Figure 8: Selecting the **Additional input file**.

Section 2.1 describes how to create the additional input (.aai) file for the amine chemistry.

The next step is to add entries for the 'AMINE#', 'NITROSAMINE#', and 'NITRAMINE#' species to the **Palette of Pollutants**, where # represents a single digit number between 1 and 9. The model code uses generic names for the types of species involved in the amine chemistry scheme so it can be applied to a variety of amines and their products. Amines and their products are grouped by the number at the end of their respective names. All 3 species must be added to the palette for any amine which is to be modelled. So, for example, if two amines 'AMINE1' and 'AMINE3' were to be modelled then the following pollutants must be added to the palette 'AMINE1', 'NITRAMINE1', 'NITROSAMINE1', 'AMINE3', 'NITRAMINE3' and 'NITROSAMINE3'. Kinetic information for 'AMINE1' and 'AMINE3' would also need to be entered in the **Amine species** section of the *.aai* file.

To add these species to the pollutant palette click on the **Data...** button in the **Palette** section of the **Setup** screen. This brings up the **Palette of Pollutants** screen shown in **Figure 9**.

*It is possible to output concentrations of the amino radical, in order to do this the corresponding RADICAL# will need to be added to the **Palette of Pollutants**.*

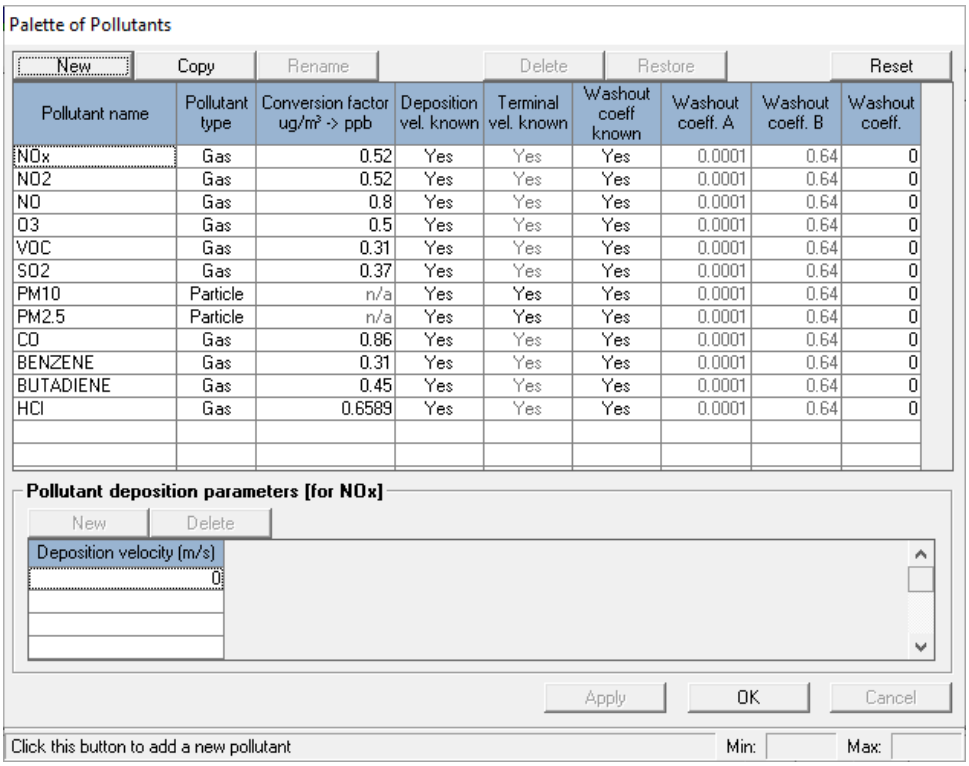

Figure 9: **Palette of pollutants**.

Clicking on the **New** button creates a new pollutant, enter the name of the pollutant and click **OK**, refer to Figure 10.

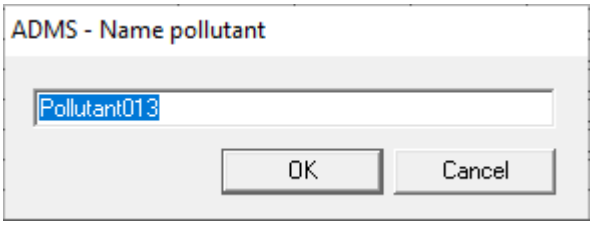

Figure 10: **Name pollutant** screen.

This step must be performed three times per amine to create the additional rows for the three amine chemistry species. The data for each of the species can then be entered by clicking in each cell and typing the names or values as appropriate.

*Note that the species must strictly be named '**AMINE#**', '**NITROSAMINE#**' and '**NITRAMINE#**', where # is a single digit number between 1 and 9. For any amine species which is to be modelled all 3 pollutants must be specified. Even if an amine doesn't form a stable nitrosamine the corresponding '**NITROSAMINE#**' should still be entered into the **Palette of Pollutants** for that amine.*

Values for the conversion factor from µg/m^3 to ppb are required for each of the species involved. The conversion factors are entered by clicking on the cell and typing the particular value for that species. The values are dependent on the particular amine

being modelled. The pollutant type should be left as **Gas** and all the other parameters in the palette can remain as their default values.

Figure 11 shows an example of the pollutant palette after completion for AMINE1.

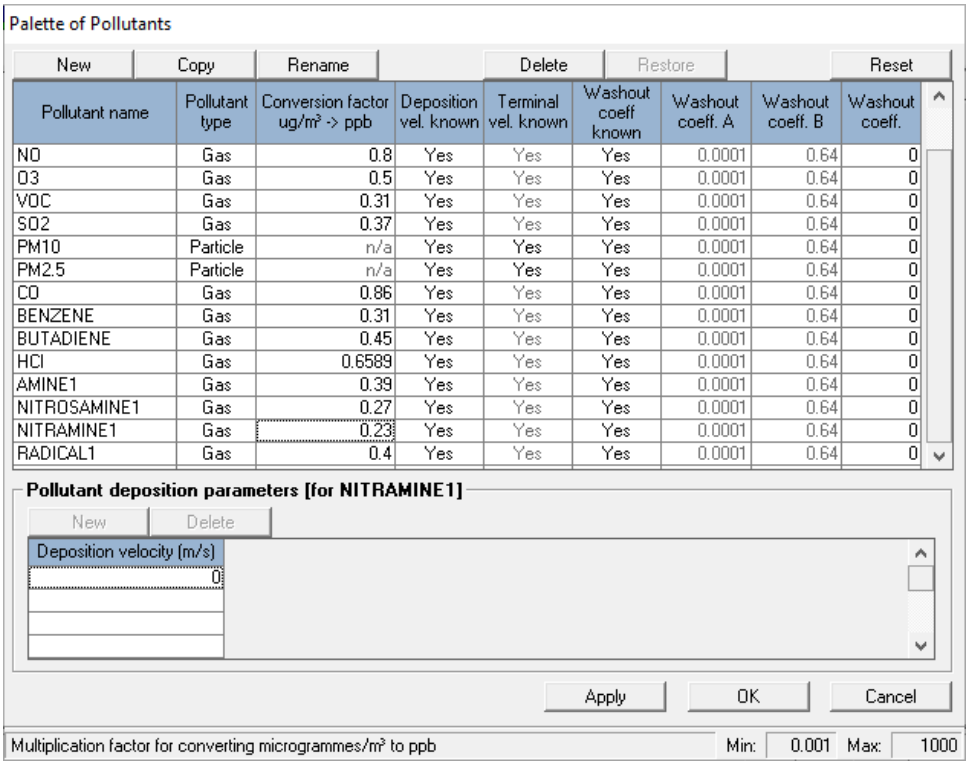

Figure 11: Completed **Palette of pollutants** with an amine species added.

*If the same set of amine species are to be used in multiple runs it may be convenient to **Export** the **Palette of pollutants** to a* .ptt *file which can then be imported into future runs.*

2.2.2 Source screen

Once the data for each of the amine species has been entered into the model the emissions data for each of the sources can be specified. The source information can be entered as usual, refer to Section 3.2 of the ADMS 6 User Guide for information about this. In the **Source** screen of the ADMS 6 interface (shown in **Figure 12**) click on the **Emissions** button to bring up the emissions screen shown in **Figure 13**.

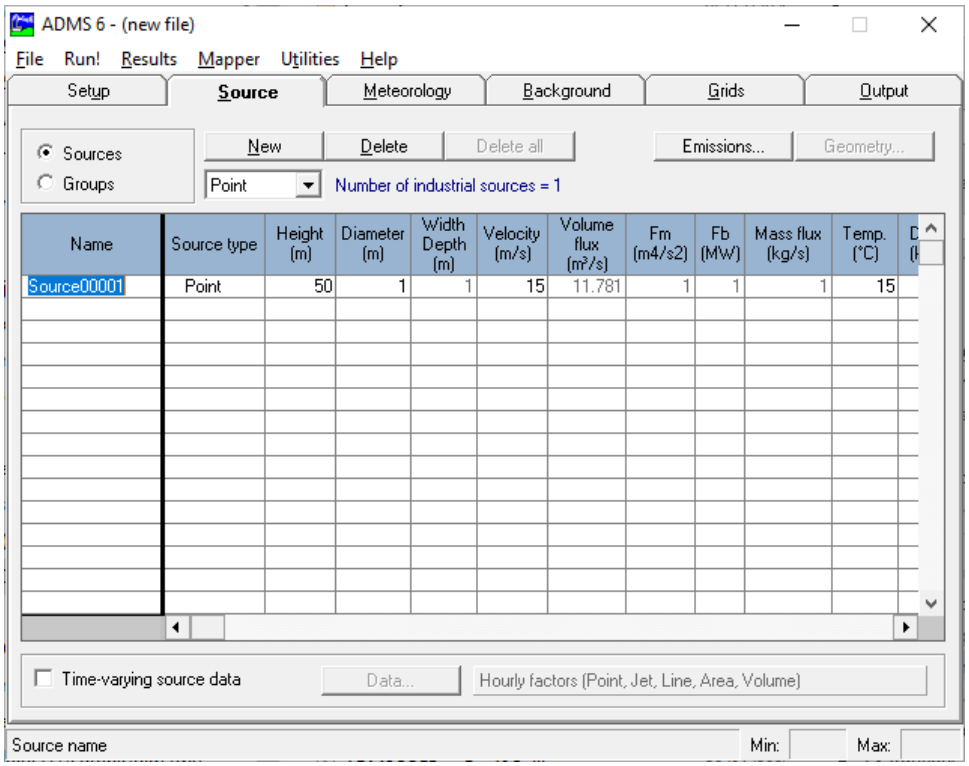

Figure 12: The **Source** screen in ADMS 6.

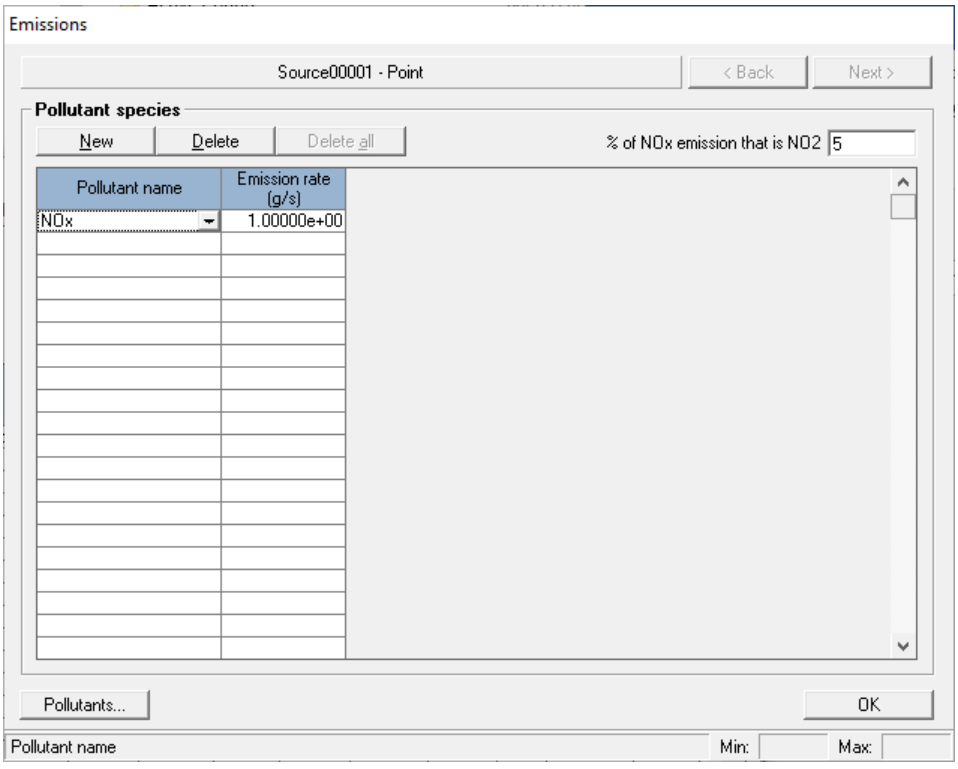

Figure 13: The **Emissions** screen.

Click on **New** to add a new pollutant and then use the drop down arrow to select **AMINE#** from the list. An emission rate for the amine can be entered in g/s by clicking on the emission rate cell and typing the value.

Likewise, emissions can also be specified for **NITROSAMINE#** and/or **NITRAMINE#**, if directly-emitted nitrosamines and nitramines are to be modelled. To add emission rates for these or other additional species first click on **New** in the emissions screen and then select the pollutant species and enter the emission rate as usual.

*Note that each **AMINE#** and **NOx** must be emitted by at least one source in order for the chemistry to be modelled. If the **Creation of unstable nitrosamines** option is selected for an amine then there can be no emissions of the corresponding nitrosamine.*

An example emissions screen is shown in **Figure 14**.

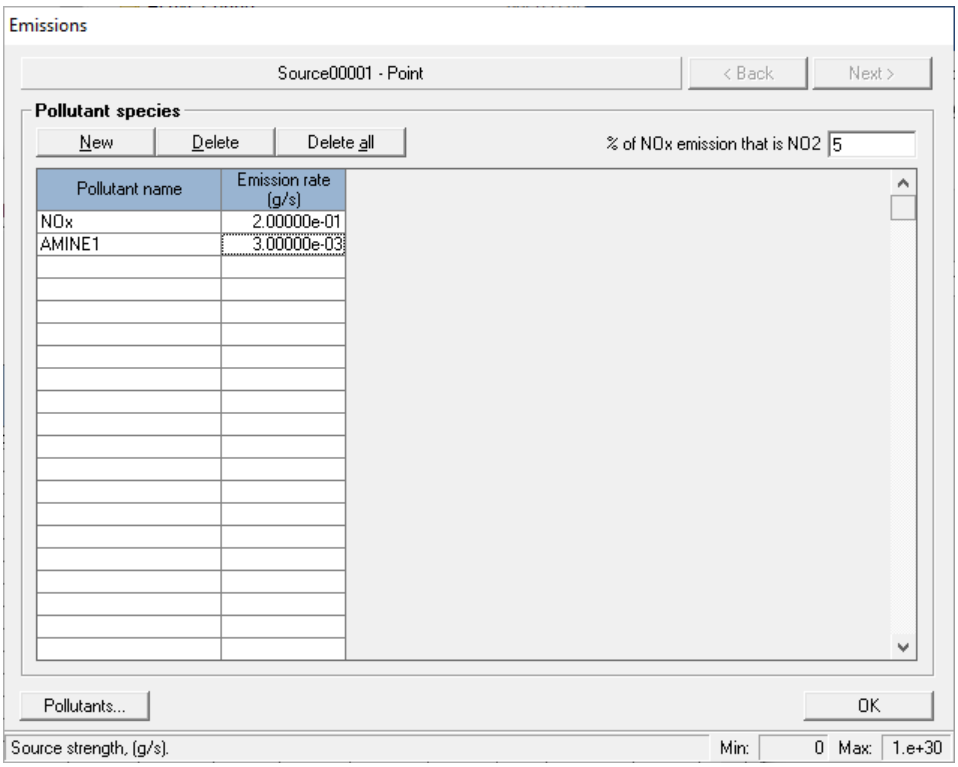

Figure 14: Example **Emissions** screen.

2.2.3 Background screen

When chemistry is being modelled in ADMS 6, ambient background concentration values for the species involved must be entered via the **Background** screen in the interface, see **Figure 15**.

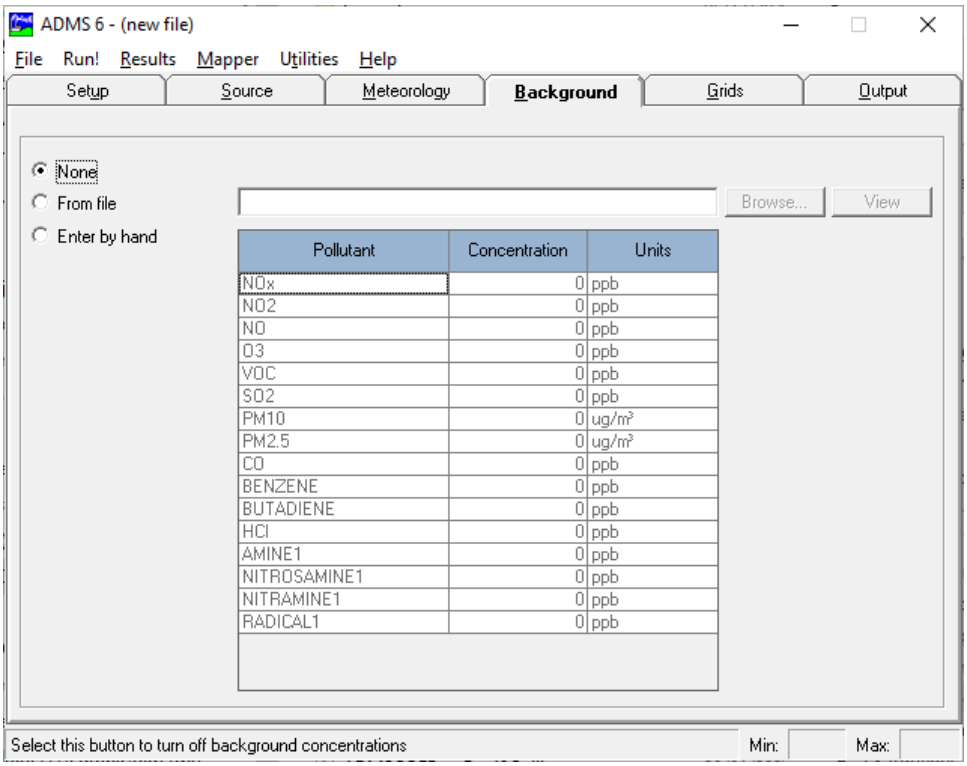

Figure 15: The **Background** screen in ADMS 6.

Ambient values must be entered for the NO_x species (i.e. NO_x, NO_2) and ozone (O_3). The values for the amine chemistry species (AMINE#, NITROSAMINE# and NITRAMINE#) should be set to zero. Please refer to Section 3.4 of the ADMS 6 User Guide for further details about how to enter background data in ADMS 6.

It is strongly recommended to use hourly varying background values from a .bgd file.

2.2.4 Output screen

The output for the amine chemistry species must be specified in the Output screen of the ADMS 6 interface. To add a pollutant to the output table first click on **New** and then select the required pollutant from the list under **Name**. Options for short/long-term output; averaging details; percentiles and exceedences; and units for output are all specified in the same way as other pollutants modelled in ADMS 6, as described in Section 3.6 of the ADMS 6 User Guide. **Figure 16** shows an example output screen for a run including amine chemistry.

*When modelling amine chemistry it is possible to include up to 80 pollutants for output in the **Pollutant output** table of the **Output** screen.*

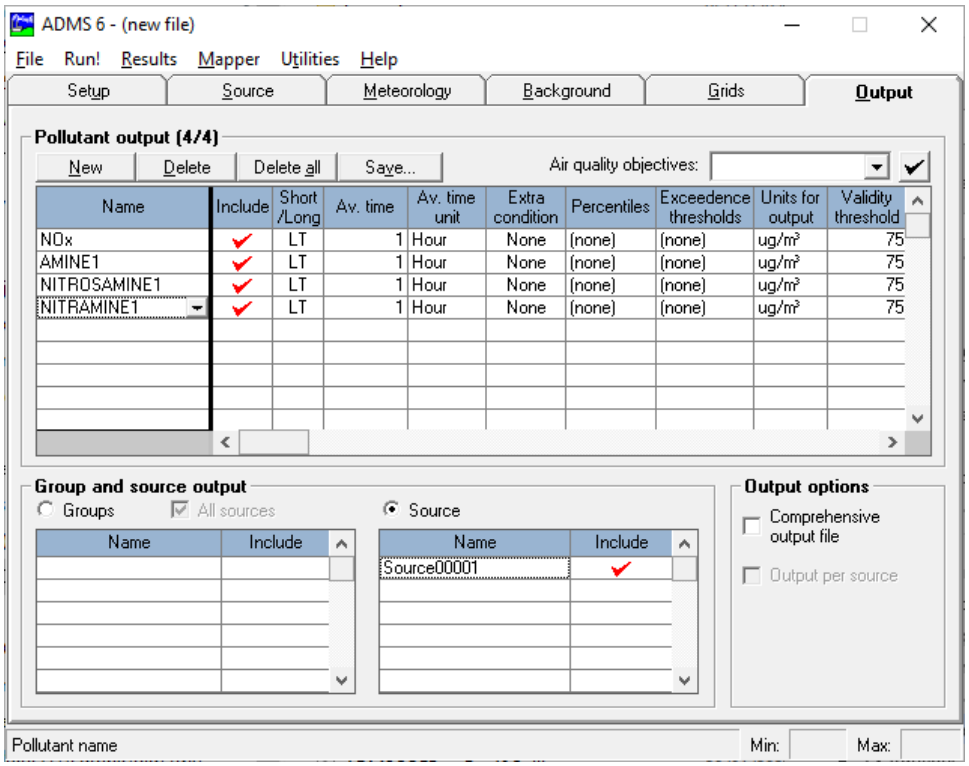

Figure 16: Example output for an amine chemistry run.

To run the model save the ADMS 6 *.apl* file and click on **Run!** in the menu options at the top of the interface.

2.3 Aqueous amine scheme

ADMS 6 includes the ability to incorporate the absorption of the amines and their products into any liquid water within the plume. This option uses Henry's law to partition the amine and their products based on the liquid water in the plume as calculated by the plume visibility module. Instructions on how to enter the Henry's law parameters are given in Section 2.3.1 and details on settings required in the ADMS 6 interface are given in Section 2.3.2. There is also an additional option to include the effects of droplet nucleation around salt particles in the calculations of the water content. Details on this option are given in Section 2.3.3.

2.3.1 Setting up the .aai file

To enable the aqueous amine chemistry scheme check the **Aqueous amine scheme** box on the **Amine chemistry** screen in the **Additional input file editor**, **Figure 3**. The following parameters then need to be entered for each amine species included in the run:

- **Amine species**, the name of the amine species in the form 'AMINE#' where # is a single digit between 1 and 9,
- **H_amine**, the Henry's law constant for that amine in mol/L/atm
- **H_nitrosamine**, the Henry's law constant for the corresponding nitrosamine in mol/L/atm
- **H_nitramine**, the Henry's law constant for the corresponding nitramine in mol/L/atm

Care should be taken to ensure that the Henry's law constants are entered in the correct units, some sources quote the inverse of the quantities required here.

2.3.2 Settings in the ADMS 6 interface

When modelling using the aqueous amine scheme it is necessary to also switch on the **Plume visibility** module in the **Setup** screen of the ADMS 6 interface in order for the model to be able to calculate plume water content. The plume visibility option requires the **Mass H2O (kg/kg)** emission rate to be specified for each source and a measure of humidity to be specified in the meteorological data. Full details of using the **Plume visibility** module are given in Section 4.5 of the *ADMS 6 User Guide*.

The emissions and output concentrations given by the amine pollutants described in Section 2.1.2, i.e. 'AMINE#', 'NITRAMINE#' and 'NITROSAMINE#' represent the combined total of the aqueous and gaseous phases of their corresponding species. For output concentrations it is possible to get the aqueous or gaseous phase concentrations separately. To do this additional pollutants should be added to the **Pollutant palette** with '_Gas' or '_Aq' added to the name and then output for those pollutants requested on the output screen. So for instance if the gaseous and aqueous phase concentrations are required for 'AMINE1' then 'AMINE1_Gas' and 'AMINE1_Aq' should be added to both the **Pollutant palette** and the **Output** screen.

The '_Gas' and '_Aq' components are only available for output, emissions must always be for the total pollutant.

2.3.3 Droplet nucleation

By default the aqueous amine scheme uses the standard ADMS 6 approach to calculating liquid water content within the plume visibility module which is based on the ambient saturation level. For highly soluble amines even a small liquid water content can effect the chemistry calculations. To account for other mechanisms which can generate liquid water within the plume there is a droplet nucleation option.

To use the droplet nucleation method the aqueous amine scheme should be enabled and then in the **Plume visibility** section of the **Additional input file editor** enable the **Plume droplets** option, **Figure 17**.

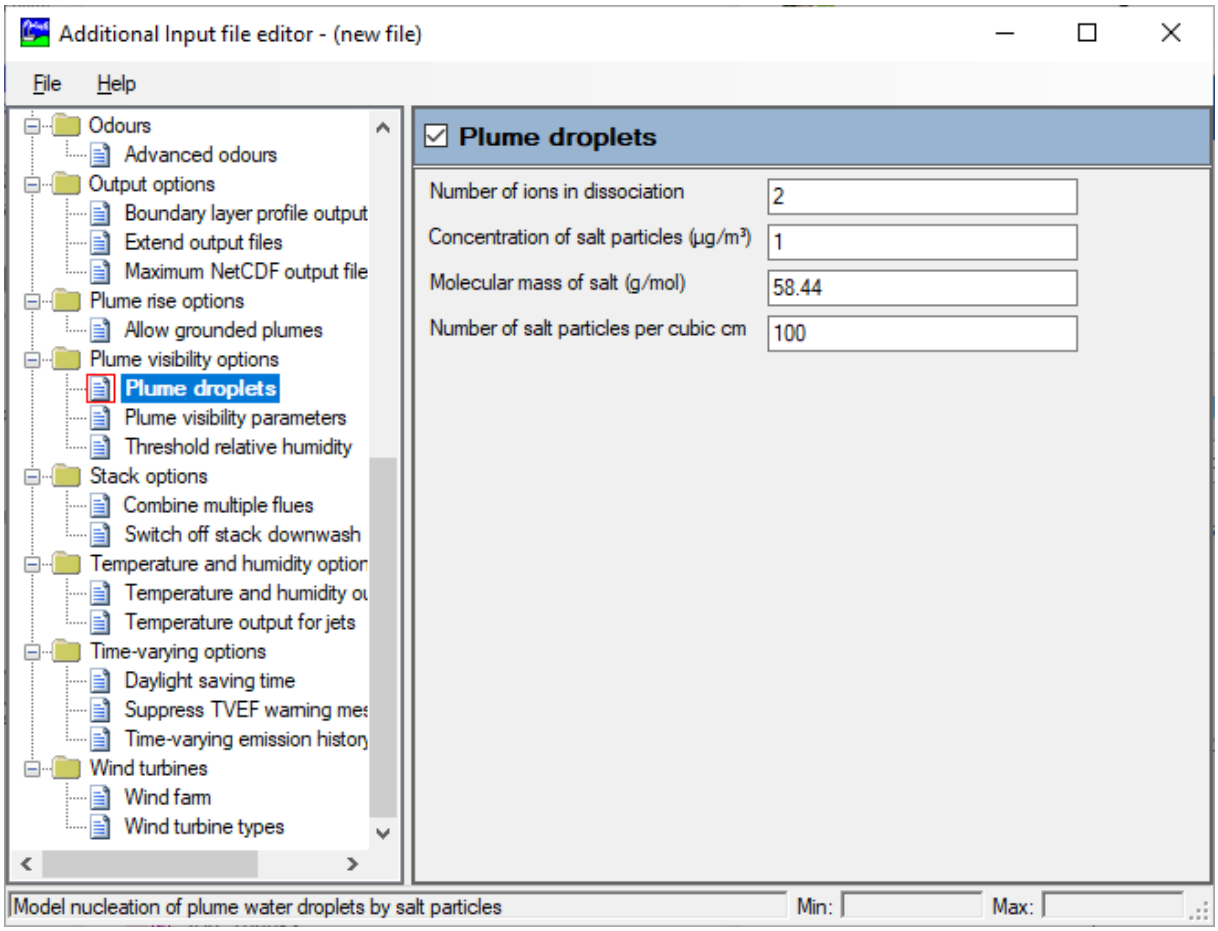

Figure 17: **Plume droplets** option in the **Additional Input File editor**.

On this screen there are four parameters to enter:

- **Number of ions in dissociation**, the number of ions into which the salt dissociates, e.g. 2 for NaCl
- **Concentration of salt particles (µg/m³)**, the concentration of salt particles in the atmosphere
- **Molecular mass of salt (g/mol)**, the molecular mass of the salt particles, e.g. 58.44 g/mol for NaCl
- **Number of salt particles per cubic cm**, the number of salt particles per cubic centimetre in the atmosphere.

2.4 Modelling washout

ADMS 6 includes the ability to calculate the effect of rainfall induced washout on the concentrations of amines and their products. This option only calculates the depletion effect on concentration, it does not calculate any deposition values. A method for calculating deposition with amine chemistry is given in Section 2.5.2.

2.4.1 Setting up the .aai file

To enabling the modelling of washout check the **Amines washout** option in the **Amines chemistry** screen of the **Additional input file editor**, **Figure 3**.

2.4.2 Settings in the ADMS 6 interface

Although the **Wet deposition** option must not be switched on in the **Setup** screen of the ADMS 6 interface, appropriate washout coefficient parameters must be entered in the **Pollutant palette** for every amine species and their products if the **Amines washout** option is enabled. These can be fixed or rainfall dependent, see Section 4.3 of the ADMS 6 User Guide for more details. These washout coefficients are applied to the gaseous phase when modelling the aqueous amine scheme or the whole concentration if not using the aqueous amine scheme. Washout coefficients for the aqueous phase when modelling with the aqueous amine scheme are calculated automatically based on the droplet sizes.

If any pollutant has **Washout Coeff known** set to **No**, or if the aqueous amine scheme is being modelled then it is also necessary to specify the rainfall rate as part of the meteorological data.

2.5 Modelling tips

2.5.1 Calculating a value of c

The user needs to specify, c, the parameter used in calculating the hourly varying hydroxyl radical concentrations. One way of determining a value for this parameter is based on annual average values for j_{NO_2}, ozone and hydroxyl radical concentrations.

To calculate an annual average value of j_{NO_2}, follow this procedure:

- Create a Meteorological output (*.mop*) file by running a simple (non-amine) run in ADMS 6 using your meteorological data;
- Locate the column labelled 'K' – this contains the values for the incoming solar radiation (in W/m^2);
- Using these values of K, calculate j_{NO_2} using the following relationship, which is used by ADMS 6 (as described in document P18/02 of the ADMS 6 Technical Specification):

$$j_{NO_2} = 8 \times 10^{-4} \exp\left(-\frac{10}{K}\right) + 7.4 \times 10^{-6} K \quad K > 0$$
$$j_{NO_2} = 0 \quad K = 0$$

- For each hour then calculate [O$_3$]$* j_{NO_2}$ where [O$_3$] is in ppb
- Calculate the annual average of these [O$_3$]$* j_{NO_2}$values, $\overline{[O_3]j_{NO_2}}$.
- Calculate c using this value and the annual average value of the hydroxyl radical ($[OH]$) in ppb using

$$c = \frac{[OH]}{\overline{[O_3]j_{NO_2}}}.$$

2.5.2 Calculating deposition of amines and their products

If dry and/or wet deposition output is required for the amines and their products, the following method can be applied:

Carry out three model runs:

- Run (1): With amine chemistry switched on, as required
- Run (2): Run with the same model setup as Run (1), but with the amine chemistry switched off and the deposition output switched on. New pollutants can be created in the **Pollutant Palette** to represent the depositing pollutants of interest (e.g. called 'DEP_NITROSAMINE#' and 'DEP_NITRAMINE#'). Suitable deposition parameters can be assigned to each of these pollutants.

- Run (3): The same run as in (1) and (2), but with both amine chemistry and deposition output switched off

From a combination of the output from Runs (2) and (3), values for the ratio of the concentration to deposition flux can be calculated at each location.

The concentrations output from Run (1) can then be post-processed using these ratios to give values of deposition fluxes at each location.

The deposition fluxes can be determined from:

$$D = C_1.\left(\frac{D_2}{C_3}\right)$$

Where:

- D is the deposition flux required (for the nitrosamines and/or nitramines);
- C_1 is the output concentration from Run (1);
- D_2 is the output deposition flux from Run (2);
- C_3 is the output concentration from Run (3).

2.5.3 Other parameters of importance for amine chemistry

The concentrations of nitrosamines and nitramines are highly dependent on the latitude, due to changes in solar radiation and thus the rate of photolysis of the nitrosamines and NO_2. This is in addition to the general effects on dispersion. It is important, therefore, to set the latitude to an appropriate value in the ADMS meteorology screen. Please refer to Section 3.3 of the ADMS 6 User Guide for further details.

SECTION 3 Technical summary

3.1 Reaction equations

The rate expressions used in the model for the amine chemistry scheme described in Section 1.1 are taken from the Atmospheric Degradation of Amines (ADA) report published by the Norwegian Institute for Air Research (NILU) as part of the Climit project (Nielsen *et al*., 2011). The generic names AMINE, NITROSAMINE, etc. are used below, however these equations are solved for each of the amine species being modelled.

1. Loss of the AMINE

$$\frac{d[AMINE]}{dt} = -k_1[AMINE][OH]$$

2. Production of the amino RADICAL

$$\frac{d[RADICAL]}{dt} = k_{1a}[AMINE][OH] + j_5[NITROSAMINE] - k_2[RADICAL][O_2] - k_3[RADICAL][NO] - k_4[RADICAL][NO_2]$$

3. Production of NITRAMINE

$$\frac{d[NITRAMINE]}{dt} = k_{4a}[NO_2][RADICAL]$$

4. Production of NITROSAMINE

$$\frac{d[NITROSAMINE]}{dt} = k_3[RADICAL][NO] - j_5[NITROSAMINE]$$

Here k_i are the reaction rate constants for the relevant amine species, where the subscript i relates to the number of the relevant chemical equation (1a) – (4) given in Section 1.1, and j_5 is the rate constant for the nitrosamine photolysis, also amine species dependent. A quantity in square brackets [X] represents the concentration of that species.

The hydroxyl radical concentration [$^{\bullet}$OH] is the same for each amine species and is modelled by the equation

$$[OH] = c[O_3]j_{NO_2}$$

where c is a constant and j_{NO_2} is the rate constant for the nitrogen dioxide photolysis.

3.2 General description of the ADMS 6 amine chemistry scheme

The reaction scheme for the amine chemistry calculates concentrations at output locations using the following procedure, where it is assumed that the **Low concentration dilution and entrainment** option has also been selected:

1. Dispersion is calculated along an internal grid storing the plume sizes at each step along the internal grid using the standard ADMS dispersion algorithms;
2. The concentrations and age of the primary pollutants are calculated at each receptor point using the standard ADMS dispersion algorithms;
3. The primary concentrations are adjusted to remove dilution effects using the ratio of the plume spread at $t = 0$ to $t = t_{age}$, i.e. $\frac{(\sigma_y \sigma_z)_{t=0}}{(\sigma_y \sigma_z)_{t=t_{age}}}$;
4. The chemical reaction equations are applied over a time δt to all pollutants;
5. The concentrations of all pollutants are diluted as ambient air, containing the background pollutants, is entrained into the plume. The rate of dilution is given by the ratio of the plume spread at the beginning and end of this time step;
6. Steps 3 and 4 are repeated for each time step, δt, until $t = t_{age}$;

3.3 Modelling of the aqueous amine scheme

The reaction scheme for the calculations when the **Aqueous amine scheme** option is selected is as follows:

1. Dispersion is calculated along an internal grid storing the plume sizes and liquid water content at each step along the internal grid using the standard ADMS dispersion and plume visibility algorithms;
2. The concentrations and age of the primary pollutants are calculated at each receptor point using the standard ADMS dispersion algorithms;
3. The primary concentrations are adjusted to remove dilution effects using the ratio of the plume spread at $t = 0$ to $t = t_{age}$, i.e. $\frac{(\sigma_y \sigma_z)_{t=0}}{(\sigma_y \sigma_z)_{t=t_{age}}}$;
4. The pollutants are partitioned into gaseous and aqueous phases based on the amount of liquid water in the plume at that time;
5. The chemical reaction equations are applied to the gaseous phase over a time δt to all pollutants;
6. The concentrations of all pollutants are diluted as ambient air, containing the background pollutants, is entrained into the plume. The rate of dilution is given by the ratio of the plume spread at the beginning and end of this time step;
7. Steps 3, 4 and 5 are repeated for each time step, δt, until $t = t_{age}$;
8. If gaseous or aqueous phase concentrations are requested for output a final partitioning is carried out, if there is still liquid water in the plume at the receptor.

At each stage the fraction of the pollutant that is in the gaseous phase is calculated as:

$$C_g^{PPB} = C_0^{PPB}(1 + \alpha \rho_{air} \kappa H)^{-1}$$

where C_g^{PPB} and C_0^{PPB} are the gaseous and total concentration of a particular pollutant in ppb, α is the liquid water content in kg of water per kg of dry air, ρ_{air} is the density of air (which will always be taken as 1.225 kg/m^3 regardless of the amount of water in the air), $\kappa = 2.4041471 \times 10^{-2}$, and H is the Henry's law constant for that pollutant in mol/L/atm.

3.3.1 Droplet nucleation

By default the plume liquid water content for the aqueous amine scheme is calculated following the standard ADMS plume visibility methodology. This methodology is based on comparing the liquid water in the plume to the saturation level, see Section 9.14 of the ADMS 6 User Guide. The Droplet nucleation option allows for the effects of liquid droplets nucleating around salt particles to also be taken into consideration. This has the effect of increasing the liquid water content at low water levels.

The liquid water content, LWC, from the droplet nucleation method is calculated as:

$$LWC = \frac{4N\rho_w \pi r^3}{3\rho_a}$$

Where ρ_a is the density of air (in g/cm^3), ρ_w is the density of water (in g/cm^3), N is the number of salt particles per cm^3 and r is the droplet radius in cm calculated from the Köhler equation governing the equilibrium between an aqueous solution drop and humid air (Eqn (6-29) of *Pruppacher and Klett (1980)*), namely:

$$r^3 \ln\left(\frac{R}{100}\right) - Ar^2 + B = 0$$

where R is the relative humidity and A and B are constants calculated below.

A is calculated from the temperature, T, in kelvin as:

$$A = \frac{3.3 \times 10^{-5}}{T}$$

B is calculated from the user input parameters as:

$$B = \frac{4.3\nu C_s}{NM_s}$$

With ν the number of ions for dissociation, C_s the concentration of salt converted to g/cm^3, N the number of salt particles per cm^3 and M_s the molecular mass of salt in grams per mole.

3.4 Modelling of washout

The Amines washout option allows for the effect of rainfall induced washout on the concentration of amines and their products. This option only calculates the depletion effect on airborne concentration, it does not calculate any amounts deposited to the ground. When this option is being used, at each stage in the chemistry calculations the concentration for each pollutant is multiplied by $e^{-\Lambda\delta t}$ where Λ is the appropriate washout coefficient for that phase. If the aqueous amine scheme is being modelled this factor is also applied to the liquid water in the plume.

For the gaseous phase, or the whole release if the aqueous amine scheme is not being modelled, the washout coefficient is calculated from the information entered in the pollutant palette for that species, taking into account the rainfall if required. For the aqueous phase and liquid water content the washout coefficient is calculated based on the precipitation rate by assuming a constant droplet radius.

SECTION 4 References

This is the reference list for this User Guide.

Låg M, Lindeman B, Instanes C, Brunborg G, Schwarze P. Health effects of amines and their derivatives associated with CO2 capture. The Norwegian Institute of Public Health, 2011 ISBN 978-82-8082-462-2

Nielsen et al, "Atmospheric Degradation of Amines (ADA). Summary Report: Photo-oxidation of Methylamine, Dimethylamine and Trimethylamine". Climit project no. 201604. Norwegian Institute for Air Research. January, 2011

Pruppacher and Klett, Microphysics of Clouds and Precipitation, Reidel ,1980 ISBN: 978-0-306-48100-0

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